

USE OF A POLYFUNCTIONAL SURFACE-ACTIVE COMONOMER AND OTHER AGENTS TO IMPROVE ADHESION BETWEEN A RESIN OR COMPOSITE MATERIAL AND A SUBSTRATE

BACKGROUND OF THE INVENTION

The invention described herein was made in the course of work under a grant or award from the Department of Health, Education and Welfare.

This invention relates to the field of improving adhesion between a resin or composite material and a solid surface capable of binding polyvalent cations. Such surfaces include metals or alloys with oxide surfaces; glasses; microcrystalline glasses; ceramics; natural and synthetic minerals; concrete; calcified tissues; hard tissues, especially hard tooth tissues; enamel; and most preferably, dentin.

In reconstructive dentistry, composite resins are applied to the surface of remaining dentin. The need for improved adhesion of dental resin to the dentin by way of a chemical mechanism is broadly recognized, and means to obtain durable adhesive bonding of composite resins to dentin would have immediate utility in dental practice. The technique of etching enamel with acid has resulted in major advances in clinical dentistry; however, the techniques for bonding composite resins to dentin and certain enamel surfaces remain unsatisfactory. See Silverstone and Dogon (eds.), *The Acid Etch Technique* (1975).

Surface-active comonomers that are difunctional (having one chelating group and one polymerizable group per molecule) have been synthesized and tested. See Bowen, "Adhesive Bonding of Various Materials to Hard Tooth Tissues: I. Method of Determining Bond Strength," 44 *J. Dent. Res.* 690-95 (1965); Bowen, "Adhesive Bonding of Various Materials to Hard Tooth Tissues: II. Bonding to Dentin Promoted by Surface-Active Comonomer," 44 *J. Dent. Res.* 895-902 (1965). See also U.S. Pat. No. 3,635,889. These difunctional agents are to be distinguished from the polyfunctional surface-active comonomers, or "PolySACs", of the present invention, which have two or more independent sets of chelating ligand groups and at least one, but preferably two or more, vinyl, vinylidene or other groups capable of homopolymerization and copolymerization with the resin to be bonded to the dentin surface. The need for some type of polyfunctional surface-active comonomer has been recognized on the theoretical level, see Bowen, "Adhesive Bonding Of Various Materials To Hard Tooth Tissues: IX. The Concept of Polyfunctional Surface-Active Comonomers," 9 *J. Biomed. Mater. Res.* 501-10 (1975), but heretofore no specific structures for PolySACs have been proposed and no method for synthesizing PolySACs has been taught in the literature. The present invention makes such compounds available to the art for the first time.

The reactants employed in the synthesis of PolySACs are well known. The acrylates and methacrylates and epoxy acrylates and methacrylates which form the preferred precursors for PolySACs have been known and used in a number of technical fields, including the dental field. See, for example, U.S. Pat. Nos. 3,930,076; 3,628,988; 3,287,155; 3,194,783; 3,740,850; 3,539,526; 3,751,399; 4,072,592; 2,824,851; 3,719,623; 3,066,112; 3,825,518; 3,539,533 and 3,815,239. In some instances, the polymerization of these materials has been catalyzed by amine accelerators. See, for example, U.S. Pat. No.

3,740,850 to Bowen and Argentar. Carboxylic acids and their derivatives have been employed in various roles in connection with acrylates and epoxides. See U.S. Pat. Nos. 3,991,133; 3,294,865; 3,373,221; 2,947,338; 2,967,840 and 3,787,521 and 74 *Chemical Abstracts* 88756n (1971).

Reconstructive dental work is impeded not only by lack of an effective resin-dentin adhesive, but also by the presence of a smeared surface layer on dentin that has been mechanically cut and of a salivary pellicle on the surface of dentin exposed by gingival recession. While strong, polybasic acids such as phosphoric acid or citric acid of various concentrations (usually on the order of 50%) have been proposed as cleansers to be applied to enamel surfaces for periods of a minute or longer, these acids have no beneficial effect in promoting adhesion to dentin and are irritating to the dental pulp tissues. Furthermore, the removal of smeared layers or surface debris by dissolution with polybasic organic acids may result in a dentinal surface with cationic sites blocked by residual molecules or derivatives of these acids. See Bowen, "Adhesive Bonding of Various Materials to Hard Tooth Tissues: VII. Metal Salts as Mordants for Coupling Agents," in Moskowitz, H. D., Ward, G. T., and Woolridge, E. D. (eds.), *Dental Adhesive Materials*, Proceedings from Symposium Nov. 8-9, 1973 at the Hunter-Bellevue School of Nursing 205-21 (1974).

Adhesive techniques which solve these problems in the dental field may be drawn upon to beneficiate adhesion of resins or composite materials to solid surfaces capable of binding polyvalent cations in other contexts.

SUMMARY OF THE INVENTION

It is an object of this invention to provide polyfunctional surface-active comonomers which are the reaction products of an epoxy acrylate or methacrylate and an aminobenzoate.

An additional object of this invention is the use of these PolySACs as adhesives between a resin or composite material and a solid surface capable of binding polyvalent cations.

It is a further object of this invention to employ these PolySACs as dental adhesives between a resin or composite material and dentin.

It is also an object of this invention to provide a non-irritating cleanser which will effectively remove the smeared surface layers or salivary pellicle from dentin or enamel prior to reconstructive dental work. More specifically, it is an object of this invention to employ a monobasic acid of intermediate pK_a (relatively weak) and preferably isotonic concentration (relatively low concentration) to effectively remove the smeared layer or a contaminating layer.

Another object of this invention is the use of a mordant, preferably ferric chloride, to enrich a solid surface capable of binding polyvalent cations, and especially hard tooth tissues, in inorganic cations.

An important object of this invention is the provision of an integrated system for improving the adhesion of a resin or composite material to dentin in reconstructive dentistry which includes effective, nonirritating cleansing of the dentin surface, application of a mordant, and application of a PolySAC adhesion between the dentin and the resin or composite material.

The PolySACs which form one aspect of the present invention are the reaction products of an epoxy acrylate